

Many-particle resonances in excited states of semiconductor quantum dots

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Anderson impurity model for semiconductor quantum dot is extended to take into account both particle and hole branches of charge excitations. It is shown that in dots with even number of electrons where the Kondo effect is absent in the ground state, novel midgap exciton states emerge in the energy spectrum due to Kondo-type shake-up processes. The relevance of the model to heterostructures doped by transition metal impurities and to rare earth ions adsorbed on metallic surfaces is discussed.

I. INTRODUCTION

In recent years, the physics of single electron tunneling through quantum dots has been the focus of attention for experimentalists and theoreticians [1,2]. In these mesoscopic devices the features of many-body quantum systems are manifested, and modern technologies allow experimentalists to model various realizations of strongly correlated electron systems, even those which are hardly achievable in "natural" objects (metallic and semiconductor compounds).

Within this context, one of the most remarkable manifestations of collective quantum effects is resonance electron tunneling through quantum dots under the condition of strong Coulomb blockade. It was shown that the physics of resonance tunneling can be formulated in terms of the Anderson impurity model for strongly correlated electrons in metals [3]. It is established that the collective resonance occurs at the Fermi level, provided the Anderson impurity can virtually be regarded as a localized spin. This condition is fulfilled in quantum dots when the strong Coulomb blockade fixes the number of electrons N in the dot to be an odd integer. Exchange correlations of the spins of electrons in the leads with the spin of the dot electron arise in electron cotunneling. This scenario is reminiscent of the Kondo effect in metals doped by magnetic impurities. Indeed, the Kondo features recently predicted in Ref. [3] were observed in the conductance of quantum dots formed in GaAs/GaAlAs heterostructures [4] and Si-MOSFETs [5] by gate depletion techniques.

From the point of view of the conventional Anderson model, resonance scattering of the Kondo type as mentioned above is expected to be absent in even- N quantum dots with singlet ground state. Yet, we have recently

demonstrated that this expectation is not quite justified [6]. A Kondo-type cotunneling can indeed be induced by an external magnetic field in an even- N quantum dot fabricated in two-dimensional electron gas (2DEG) which is usually formed in GaAs/GaAlAs or Si/SiO₂ heterostructures. This magnetically driven Kondo tunneling arises in strong enough field when the Zeeman energy compensates the energy of excitation from a ground singlet state to a triplet exciton state.

In the present paper we consider the possibility of collective resonant effects in another type of semiconductor quantum dots (SQD). These can be fabricated in a form of nearly spherical droplets of Si [7], InAs [8,9], InP [10], CdSe [11] and, presumably, other semiconductors. Similarly to bulk semiconductors, such nanocrystals have filled "valence band" and empty "conduction band" formed by spatially quantized levels. The energy gap dividing these two groups of discrete levels is even wider than in their bulk parents, so it is natural to assume that in the ground state of such a SQD N is even.

Existence of electron and hole branches of charge excitations, as well as exciton lines in optical spectra was demonstrated in semiconductor nanocrystals. Moreover, evidences of Coulomb blockade phenomena (which is a necessary precondition for collective effects) are reported by some of the experiments cited above. Thus, the tunnel Hamiltonian for these quantum dots cannot be mapped on the standard Anderson model, since the existence of additional branches of excitations in quantum dots should be taken into account. Indeed, discrete exciton states do not show up in a conventional situation of an impurity immersed in a conduction band of a metal, even when such an impurity has internal charge degrees of freedom (e.g., rare-earth impurities with two unfilled electron shells [12]). However, long-living excitons can still exist in SQD coupled with metallic leads, since the scattering center is spatially isolated from the conduction electrons.

The question then arises, as to what kind of many-particle effects can be observed in SQD with additional electron-hole branches of excitations. Confined excitons are created by light illumination, and possible collective effects can be observed only at finite frequencies in excited states of the system.

Our goal in this paper is then to modify the conventional theory of resonance tunneling through quantum dots with odd N in the ground state for the case of SQD with even N in the ground and excited states. It is demonstrated below that collective shake-up processes lead, under certain conditions, to formation of a many-

particle midgap state, which can be observed, e.g., as an additional line in the luminescence spectra. For this purpose we adapt, in section 2, the basic tunnel Hamiltonian of quantum dot [3] to a more general case of SQD with electron and hole branches of single-particle excitations. Then, in section 3 we develop a perturbation theory for optical line shapes in SQD and demonstrate that new many-particle resonances arise in electron-hole co-tunneling through SQD with even \mathcal{N} at finite frequencies. Optical response function of a semiconductor nanocrystal is calculated and finite lifetime effects are discussed, which significantly influence the many-particle tunneling at finite frequency. Section 4 is devoted to the study of midgap excitons in SQD. Since the ground state of an even- \mathcal{N} quantum dot is a spin singlet, one should not expect radical reconstruction of its spin structure due to multiple creation of electron-hole pairs which is the key mechanism for the formation of a Kondo-ground state in the conventional theory. Besides, the finite life time of the excited state of SQD cuts effectively the infrared divergences in electron-hole pair spectrum, and one can hope that a perturbation approach allows one to encode the main features of the shake-up effect in the exciton spectrum of semiconductor nanocrystals. Section 5 is dedicated to applications of the theory developed so far. In particular, possibilities of realization of similar shake-up effects in other physical systems are discussed. The paper is then summarized in section 6.

II. MODEL HAMILTONIAN

The electronic structure of a quantum dot coupled to metallic leads is usually described by some variant of the Anderson Hamiltonian

$$H = H_d + H_b + H_t = H_0 + H_t. \quad (1)$$

where H_d is the Hamiltonian of an isolated dot which includes also pair interactions between confined electrons, H_b describes the band electrons in the leads, and H_t is the tunneling term which couples the electrons in the dot with those in the leads (regarded as metallic reservoirs).

Unlike the situation encountered in quantum dots formed by external electrostatic potential in 2DEG confined in the boundary layer of semiconductor heterostructure (HQD), the electronic spectrum of nanocrystal formed by the methods of colloidal chemistry, ion implantation or strain-induced surface growth, preserves, to some extent, the features of the parent (bulk) material. Our choice of effective tunneling Hamiltonian is based on quantum-mechanical calculations of the electronic spectra of real SQD (see, e.g. [13] and references therein), although we simplify these spectra and retain only those features which are essential for the many-particle shake-up effects in the exciton spectrum.

Another important difference from HQD, where one usually deals with a partially filled conduction band, is a huge energy gap E_g which divides the excitation spectrum from the ground (neutral) state of SQD. The magnitude of E_g in nanocrystals grows exponentially with decreasing radius of nanocrystal r_n , and substantially exceeds the corresponding gap in bulk semiconductors at, say, $r_n \sim 10 - 20$ Å. Electron and hole eigenstates of SQD can be classified in accordance with the angular symmetry of the nanocrystal, but the Brillouin zone parentage of these states can be traced by projecting the dot state ψ_i onto the bulk states $\phi_{n\mathbf{k}}$,

$$\psi_i = \sum_{n\mathbf{k}} C_{n\mathbf{k}}^i \phi_{n\mathbf{k}} \quad (2)$$

(see ref. [14]). Here the index $i = c\lambda, v\lambda$ stands for the orbital quantum numbers $\lambda = lm$ of the discrete state of confined electron (hole), n and \mathbf{k} are the band index and the wave vector of the electron in a bulk semiconductor. Both electron and hole levels ε_i are spatially quantized, and the distance $\delta\varepsilon_i$ between neighboring levels is rather large. For example, according to numerical calculations of Ref. [13], the first and second conduction levels in InP nanocrystal are derived from the bulk Γ_{6c} and L_{6c} states, respectively. Both levels are s-like, and the inter-level distance in a dot with $r_n = 10.11$ Å is $\delta\varepsilon_c = 0.343$ eV. Two first valence states in this SQD are derived from the bulk Γ_{8v} states, and both of them are doubly degenerate. Their envelope functions are of s- and p-type respectively, and the inter-level distance is $\delta\varepsilon_v = 0.089$ eV. Experimentally defined level spacings in InAs with $r_n = 32$ Å are $\delta\varepsilon_c = 0.31$ eV and $\delta\varepsilon_v = 0.10$ eV [9]. These values substantially exceed the tunneling amplitudes which couple the SQD with the leads.

As a consequence, when considering the lowest exciton states, restriction to the first conduction and valence levels $\varepsilon_{c,v}$ should be an excellent approximation. Whence, the dot Hamiltonian reads,

$$H_d = \varepsilon_c n_c - \varepsilon_v n_v +$$

$$\frac{U_c}{2} n_c (n_c - 1) + \frac{U_v}{2} n_v (n_v - 1) + H_{cv}, \quad (3)$$

where σ is the spin projection (spin 1/2 is considered), $n_c = \sum_{\sigma} d_{c\sigma}^\dagger d_{c\sigma}$ is the occupation number for the electrons at an empty conduction level, $n_v = \sum_{\sigma} \bar{n}_{v\sigma} = \sum_{\sigma} d_{v\sigma} d_{v\sigma}^\dagger$ is the occupation number for holes at a filled valence level ε_v . We neglect the actual four-fold degeneracy of the valence states, which is lifted in any case by Coulomb blockade. The charging energy $U_{c,v}$ which is responsible for this effect is estimated as ≈ 0.11 eV in InAs nanocrystals [9], and it is substantially larger than the tunneling width. The last term in eq. (3) describes the electron-hole interaction which lowers the energy of

the electron-hole pair and splits the exciton states into singlet and triplet ones.

The band electrons in the left and right leads are labeled by the index $\alpha = L, R$, respectively, thus the band Hamiltonian reads

$$H_b = \sum_{k\sigma} \sum_{\alpha=L,R} \varepsilon_{k\alpha} c_{k\sigma\alpha}^\dagger c_{k\sigma\alpha}. \quad (4)$$

Here the sum over k runs over the conduction band whose width D is rather large (see below). The SQD is tuned in such a way that the Fermi level ε_F (which is taken as the reference zero energy) falls into the energy gap of the quantum dot, $E_g = E_c - E_v$. Finally, the tunneling term in the Hamiltonian (1) has the usual form

$$H_t = \sum_{k\sigma\alpha} \sum_{j=c,v} (V_j^\alpha c_{k\sigma\alpha}^\dagger d_{j\sigma} + \text{h.c.}), \quad (5)$$

where $V_{(c,v)}^\alpha$ are the corresponding tunneling amplitudes (we neglect the k -dependence of these integrals). In the strong interaction regime on which we focus our attention, the tunnel width $\Gamma_i^\alpha = \pi\rho_0|V_i^\alpha|^2$ is, in general, rather small and different charge states of the SQD are not mixed by tunneling.

Having thus specified the precise form of the Hamiltonian it is useful at this point to recall the hierarchy of energy parameters in SQD, that is,

$$D, E_g > \delta\epsilon_i > U \gg \Gamma_i^\alpha. \quad (6)$$

With these data at hand, anticipating the use of perturbation theory for strongly correlated electrons [15], it is useful to rewrite the reduced dot Hamiltonian H_d in a diagonal form by means of Hubbard projection operators $X^{\Lambda\Lambda'} \equiv |\Lambda\rangle\langle\Lambda'|$,

$$H_d = \sum_{\Lambda} E_{\Lambda} X^{\Lambda\Lambda}, \quad (7)$$

where E_{Λ} are the energy levels of the dot corresponding to different occupation numbers $\{n_c, n_v\}$. The lowest levels are $E_{1,0} = E_c$, $E_{0,1} = E_v$, $E_{1,1} = \Delta$, $E_{2,0} = 2\Delta_c + U$, $E_{0,2} = 2\Delta_v + U$. Here $\Delta_c = \varepsilon_c - \varepsilon_F$, $\Delta_v = \varepsilon_F - \varepsilon_v$, $\Delta = E_g - U_{cv}$ is the energy of the lowest exciton state, which is obtained after discarding the exchange splitting \sim several meV [13] between the singlet and triplet states. The electron-hole attractive interaction is estimated as $U_{cv} \approx 0.2$ eV in InP nanocrystals [13,14].

The tunnel operator H_t changes the number of electrons in a quantum dot, hence it is convenient to rewrite it in terms of projection operators $X^{\Lambda\Lambda'}$, but first we rationalize it by making a transformation to standing wave basis [3,6]. Dropping the ubiquitous k dependence the transformation reads,

$$\begin{aligned} c_{j\sigma+} &= u_j c_{\sigma L} + w_j c_{\sigma R} \\ c_{j\sigma-} &= w_j c_{\sigma R} - u_j c_{\sigma L} \end{aligned} \quad (8)$$

Here $u_j = V_j^L/V_j$, $w_j = V_j^R/V_j$, $V_j = \sqrt{|V_j^L|^2 + |V_j^R|^2}$. Only the operators $c_{kj\sigma+}$ enter the tunnel Hamiltonian which now assumes the simple form

$$H_t = \sum_{k\sigma\alpha} \sum_{j=c,v} (V_j c_{kj\sigma+}^\dagger d_{j\sigma} + \text{H.c.}) \quad (9)$$

Hereafter it is assumed that the SQD coupling to the leads is symmetric, that is, $V_j^L = V_j^R = V_j$, $c_{kj\sigma} = c_{k\sigma}$. Now, starting with the "vacuum" state $|0\rangle$ of quantum dot in a configuration $\{0, 0\}$ and filled Fermi sea, we find that H_t connects this state with a singlet exciton state $|es\rangle = \{1\sigma, 1\sigma\}$ via the intermediate states $|kc\rangle$, $|kv\rangle$ with one electron or one hole in the dot respectively. These normalized states can be introduced as follows,

$$|kc\rangle = \frac{1}{\sqrt{2}} \sum_{\sigma} d_{c\sigma}^\dagger c_{k\sigma} |0\rangle, \quad |kv\rangle = \frac{1}{\sqrt{2}} \sum_{\sigma} c_{k\sigma}^\dagger d_{v\sigma} |0\rangle, \quad (10)$$

$$|es\rangle = \frac{1}{\sqrt{2}} \sum_{\sigma} d_{c\sigma}^\dagger d_{v\sigma} |0\rangle \equiv B^\dagger |0\rangle. \quad (11)$$

The tunnel Hamiltonian can then be expressed via projection operators

$$\begin{aligned} H_t &= V_c \sum_k \left(|kc\rangle\langle 0| + \frac{1}{\sqrt{2}} |kv\rangle\langle es| \right) + \text{H.c.} \\ &+ V_v \sum_k \left(|kv\rangle\langle 0| - \frac{1}{\sqrt{2}} |kc\rangle\langle es| \right) + \text{H.c.}, \end{aligned} \quad (12)$$

with matrix elements given by

$$\begin{aligned} \langle 0|H_t|kc\rangle &= \sqrt{2}\langle kv|H_t|es\rangle = V_c \\ \langle 0|H_t|kv\rangle &= -\sqrt{2}\langle kc|H_t|es\rangle = V_v^*. \end{aligned} \quad (13)$$

It is worth noting that the triplet exciton states

$$|et, \sigma\rangle = d_{c\sigma}^\dagger d_{v, -\sigma} |0\rangle, \quad |et, 0\rangle = \frac{1}{\sqrt{2}} \sum_{\sigma} \sigma d_{c\sigma}^\dagger d_{v\sigma} |0\rangle \quad (14)$$

are coupled to the above states only in higher orders of perturbation theory.

III. PERTURBATION THEORY FOR OPTICAL LINE SHAPE

In this section the basic equations of perturbation theory modified for excited states of SQD are derived. Evidently, no Kondo coupling is expected in the ground state Ψ_G , and the strong Hubbard repulsion U suppresses double occupation of electron or hole levels. Hence, only states with singly charged dot are admixed by tunneling to the neutral state $|0\rangle$ of the isolated dot. One

can consider this admixture as a small second order perturbation, which results in a trivial shift of the ground state energy $\delta E_G \sim -\Gamma \ln(D/E_g)$. We will see, however, that Kondo-like processes do develop in the spectrum of *electron-hole excitations* of the quantum dot given by the operator $B^\dagger = |es\rangle\langle 0|$. These states can be excited by means of photon absorption process, which is described by the Hamiltonian

$$H' = \sum_{i \neq j} \sum_{\sigma} P_{ij} d_{i\sigma}^\dagger d_{j\sigma} \exp(-i\omega t) + h.c. \quad (15)$$

Here P_{ij} is the matrix element of the dipole operator \hat{P} .

The optical line shape at photon energy $h\nu$ is given by the Kubo-Greenwood formula ,

$$W(h\nu) \simeq \text{Im} \frac{1}{\pi} \langle s | \hat{P} \hat{R}(h\nu) \hat{P} | s \rangle \quad (16)$$

where $\hat{R}(z) = (z - H)^{-1}$, and $\langle s | \dots | s \rangle$ means averaging the initial state over the equilibrium ensemble. We use the temperature perturbation theory based on the Brillouin-Wigner expansion for the resolvent

$$R(z) = (z - H)^{-1} = R^{(0)} \sum_{n=0}^{\infty} [H_t R^{(0)}]^n, \quad (17)$$

where $H_0 = H - H_t$, $R^{(0)} = (z - H_0)^{-1}$ (see, e.g. [15]). This expansion should be inserted in the partition function \mathcal{Z} , which can be written in the form

$$\mathcal{Z} = \text{Tr}_d \text{Tr}_b \{ e^{-\beta H} \} = \frac{1}{2\pi i} \int_C e^{-\beta z} \text{Tr}_d \text{Tr}_b (z - H)^{-1} dz. \quad (18)$$

Here the trace is taken over the dot and band states of H_0 , and the contour C encircles all the singularities of the integrand. Carrying out the summation over the states E_b of the conduction electrons we can obtain a system of equations for the diagonal matrix elements of the reduced resolvent $R_{\Lambda\Lambda}(z)$,

$$R_{\Lambda\Lambda}(z) = \frac{1}{\mathcal{Z}_b} \sum_b \frac{e^{-\beta E_b}}{z - E_\Lambda} \langle \Lambda | \langle b | \sum_{n=0}^{\infty} [H_t R^{(0)}]^n | b \rangle | \Lambda \rangle, \quad (19)$$

projected on the low-lying states $|\Lambda\rangle = |0\rangle, |es\rangle$ of the neutral quantum dot (\mathcal{Z}_b is the partition function of the lead electrons). As a result, the problem of line-shape function (16) reduces to calculation of the retarded exciton Green function

$$G_{ee}^R(z) = -i \int dt e^{izt} \theta(t) \langle [B^\dagger(t) B(0)] \rangle. \quad (20)$$

Coulomb blockade and other restrictions imposed by the system of inequalities (6) eliminate the possible admixture of excited states with more than one electron

(hole) in the SQD. The use of standard Feynmann diagram technique is therefore impractical. However, partial summation of perturbation series is still possible employing methods of Laplace transform (20) [15,16]. Calculations to lowest order involve only the states $|kc\rangle$ and $|kv\rangle$ (10) as intermediate states in the perturbation series (19) which are admixed by the tunnel operators (13) to the ground and exciton states $|\Lambda\rangle = |0\rangle, |es\rangle$. This approximation neglects intermediate states with multiple electron-hole pairs in the leads (see, e.g., [17]). In conventional theory, it is valid at high temperatures $T > T_K$. The response function (19) can then be found from the solution of the system of equations for the matrix elements $R_{\Lambda'\Lambda}(z) = \langle \Lambda' | (z - H)^{-1} | \Lambda \rangle$, which, in this approximation, has the following simple form

$$\begin{aligned} R_{ee} &= R_e^{(0)} (1 + \Sigma_{ee} R_{ee} + \Sigma_{e0} R_{0e}) \\ R_{0e} &= R_0^{(0)} (\Sigma_{00} R_{0e} + \Sigma_{ee} R_{ee}). \end{aligned} \quad (21)$$

The structure of these equations is illustrated in Fig.1. Here $R_\Lambda^{(0)} = \langle \Lambda | (z - H_0)^{-1} | \Lambda \rangle = (z - E_\Lambda)^{-1}$ are the zero order matrix elements of the resolvent. The self energies are given by

$$\begin{aligned} \Sigma_{00} &= \Sigma_{cc}^+ + \Sigma_{vv}^-, \quad \Sigma_{ee} = (\Sigma_{vv}^+ + \Sigma_{cc}^-) / 2, \\ \Sigma_{0e} &= (\Sigma_{cv}^- - \Sigma_{vc}^+) / \sqrt{2}, \end{aligned} \quad (22)$$

where

$$\Sigma_{jl}^+ = \sum_k \frac{V_j^* V_l f_k}{z - E_c + \varepsilon_k}, \quad \Sigma_{jl}^- = \sum_k \frac{V_j^* V_l \bar{f}_k}{z + E_v - \varepsilon_k}, \quad (23)$$

in which f_k is the equilibrium distribution function for lead electrons and $\bar{f}_k = 1 - f_k$. The exciton Green function can now be extracted from equation (21)

$$R_{ee}(\epsilon) = \frac{z - \Sigma_{00}(\epsilon)}{\mathcal{D}(\epsilon)}. \quad (24)$$

The poles of this function are determined by the equation

$$\mathcal{D}(\epsilon) = \det \begin{vmatrix} \epsilon - \Sigma_{00}(\epsilon) & -\Sigma_{e0}(\epsilon) \\ -\Sigma_{0e}(\epsilon) & \epsilon - \Delta - \Sigma_{ee}(\epsilon) \end{vmatrix} = 0. \quad (25)$$

The real parts of the self energies

$$\text{Re} \Sigma_{jl}^+(\epsilon) \approx \frac{\Gamma_{jl}}{2\pi} \ln \frac{(\epsilon - \Delta_c)^2 + (\pi T)^2}{D^2}, \quad (26)$$

$$\text{Re} \Sigma_{jl}^-(\epsilon) \approx \frac{\Gamma_{jl}}{2\pi} \ln \frac{(\epsilon - \Delta_v)^2 + (\pi T)^2}{D^2}, \quad (27)$$

have sharp maxima at energies Δ_c and Δ_v respectively ($z = \epsilon + is$, $\Gamma_{jl} = \pi \rho_0 V_j^* V_l$). These peaks which are related to logarithmic singularities result in novel features in the exciton spectra (see next section). It should be emphasized, however, that the lowest order approximation is not sufficient even for qualitative description

of exciton states, because the electron-hole pair has finite lifetime. Even when the conventional mechanisms of electron-hole recombination in the dot are ineffective at the Kondo time scale, the tunnel width of confined electron and hole should be taken into account.

The processes which are involved in the formation of exciton self energies up to the 4th order are displayed graphically in Figs. 2,3. The diagram rules are obtained by straightforward generalization of the corresponding rules described by Keiter and Kimball (see Refs. [15,16]). There are four types of vertices (Fig. 2) which couple the ground and exciton states of the dot with electron-hole states (see eq. 13). The wavy lines stand for the dot propagator $R_{e,0}^{(0)}$, the solid and dashed lines correspond to the charged (electron and hole) states of the dot and excess electrons and holes in the leads respectively. The Fermi factors $f(\varepsilon)$ and $\bar{f}(\varepsilon) = 1 - f(\varepsilon)$ are respectively assigned to the conduction electron and hole lines. In the energy denominator $(z - E_\alpha)^{-1}$ corresponding to each vertical crossection of the block between two adjacent tunnel vertices, E_α is a sum of energies $\pm\varepsilon_i$ and $\pm\varepsilon_k$ with the sign \pm respectively assigned to electron and hole propagators.

The diagrams (a, b) presented in Fig. 3 are taken into account in eq. (24) for R_{ee} . Each electron-hole loop in these diagrams contains a logarithmic singularity (26) or (27). The double wavy lines in the 4th-order diagrams (b) stand for the Green's function G_{00} containing the electron-hole loops Σ_{00} and Σ_{0e} (eq. 22) in its self energy. In lowest order, exciton finite lifetime effects can be included in the theory within the non-crossing approximation (NCA) [15,16]. Such diagrams appear in 4th order of perturbation theory (diagrams (c) in Fig.3). It should be noted that in these diagrams, intermediate states include also triplet excitons.

Within the NCA, the internal propagators in the self energies (23) can be “dressed”. The corresponding integrals are then modified as follows,

$$\begin{aligned}\tilde{\Sigma}_{jl}^+(\epsilon) &= \frac{\Gamma_{jl}}{\pi} \int_{-D}^D \frac{f(\varepsilon)d\varepsilon}{\epsilon - E_c + \varepsilon - B_{jl}^+(\epsilon + \varepsilon)}, \\ \tilde{\Sigma}_{jl}^-(\epsilon) &= \frac{\Gamma_{jl}}{\pi} \int_{-D}^D \frac{\bar{f}(\varepsilon)d\varepsilon}{\epsilon + E_v - \varepsilon - B_{jl}^-(\epsilon - \varepsilon)},\end{aligned}\quad (28)$$

where B_{jl}^\pm are the integrals obtained through insertions of electron (hole) lines in the self energies of the dot. These diagrams describe damping of electrons and holes in the intermediate charged states of the dot due to multiple electron-hole pair creation in the leads. In the next section corrections related to this damping mechanism are discussed in some details.

IV. MIDGAP EXCITONS IN SEMICONDUCTOR QUANTUM DOTS

It might be instructive to start the analysis of exciton states in even- \mathcal{N} SQD by inspecting an extreme limit of completely localized hole whose wave function does not overlap with those of the lead electron states, that is, $V_v = 0$. Tunneling is possible in this case only to the empty state ε_c above the Fermi level. Consequently, the self energies $\Sigma_{\Lambda\Lambda'}$ (22) contain only the contributions Σ_{cc}^\pm . In the conventional situation [15] this case corresponds to a trivial singlet ground state with $n_c = 0$ where states with $n_{c\sigma} = 1$ are decoupled from the low-energy excitations. The second order correction Σ_{cc}^+ merely results in a trivial shift δE_0 of the *ground state* energy (see above). However, in SQD the corresponding correction Σ_{cc}^- to the *exciton energy* $\epsilon = \Delta$ has a logarithmic singularity at an energy Δ_v (see eq. 27), and the weak coupling perturbation theory becomes invalid at some characteristic “Kondo” temperature $T_K = D \exp(-2\pi\Delta_v/\Gamma_c)$. At $T > T_K$ this correction results in an additional peak in the exciton spectral function $\sim \text{Im}R_{ee}(\epsilon)$ at $\epsilon \approx \Delta_v$. Possible physical realizations related to this new type of solution are discussed in the concluding section.

Next, let us consider a more realistic (and complicated) situation when the tunneling is allowed both in electron and hole channels, but the hole state is out of resonance with the band continuum. It arises, e.g., in a device whose leads are prepared from a strongly doped n -type semiconductor with a gap located against the top of the valence band of the SQD (see Fig. 4). The pairs GaAs(lead)/InAs(dot) or CdSe(lead)/ZnTe(dot) are possible candidates for such heterostructures. One may also tune the level ε_v in the energy gap of the lead semiconductor by applying an external gate voltage. In principle, structures with damped hole and undamped electrons in the dot can also be fabricated.

Consider now an asymmetric configuration with strongly localized hole, $\Delta_v > \Delta_c$, and assume that

$$\Delta_v - \Delta_c \gg \Gamma_{c,v} \quad \eta \equiv \left(\frac{V_v}{V_c}\right)^2 \ll 1. \quad (29)$$

The second inequality reflects the known fact that hole states tend to be more confined inside the dot and more compact than electron states [18]. Again, in lowest order of perturbation theory which neglects intermediate states with electron-hole pairs in the leads the spectral density given by $\text{Im}R_{ee}(\epsilon)$ displays additional peaks along with the conventional exciton peak at $\epsilon \sim \Delta$. The latter can be obtained from eqs (24) and (25) by representing the secular equation in a form

$$\epsilon \approx \Delta + \Sigma_{ee}(\Delta) + \frac{|\Sigma_{0e}(\Delta)|^2}{\Delta}. \quad (30)$$

Note that the logarithms in the self energies (26),(27) are small at $\epsilon \sim \Delta$, so this equation merely describes a weak

renormalization of the bare exciton state $\epsilon = \Delta$ caused by virtual tunneling processes.

Novel aspects are exposed in the behavior of R_{ee} (see equation 24) at $\epsilon \sim \Delta_v$ where Σ_{ij}^- have a sharp maximum. The secular equation (25) may then be rewritten as

$$2(\epsilon - \Delta) = \Sigma_{vv}^+ + \Sigma_{cc}^- + \frac{|\Sigma_{cv}^- - \Sigma_{vc}^+|^2}{(\epsilon - \Sigma_{cc}^+ - \Sigma_{vv}^-)}. \quad (31)$$

To find the resonance solution at $\epsilon \sim \Delta_v$, note that the smooth contributions $\Sigma_{ij}^+(\epsilon)$ (26) can be neglected as compared with the singular self energies $\Sigma_{ij}^-(\epsilon)$ (27). The most singular term is estimated as $\Sigma_{cc}(\Delta_v) \sim \Delta_c/2$ (see upper panel of Fig. 5). Employing an approximate value of $\Sigma_{vv}^-(\Delta_v) \approx -\eta\Delta_c$ in the denominator of the ratio on the r.h.s., the above equation reduces to,

$$2(\epsilon - \Delta) \approx \Sigma_{cc}^- + \frac{\eta|\Sigma_{cc}^-|^2}{\Delta_v + \eta\Delta_c}. \quad (32)$$

This equation has a Kondo-like pole at $\epsilon = \Delta_v, T = \tilde{T}_K$, where

$$\tilde{T}_K = De^{-2\pi\Delta_c/\tilde{\Gamma}_c}, \quad (33)$$

and $\tilde{\Gamma}_c \approx \Gamma_c(1 - \eta\Delta_c/\Delta_v)$. As mentioned above, this pole does not imply the occurrence of a real bound state. It merely points out the characteristic temperature of crossover from the weak interaction regime to the strong coupling one. The perturbation approach is valid only at $T > \tilde{T}_K$.

Beside the resonance at $\epsilon \sim \Delta_v$ there is of course another resonance at $\epsilon \sim \Delta_c$. Repeating the above procedure, only the terms Σ_{ij}^+ are retained in equation (31), and the midgap peak is found at $\epsilon = \Delta_c$, with characteristic temperature $\tilde{T}'_K = D \exp(-2\pi\Delta_v/\tilde{\Gamma}_v)$, with $\tilde{\Gamma}_v \approx \Gamma_v\eta\Delta_c/\Delta_v$. Since $\tilde{T}'_K < \tilde{T}_K$, this peak is noticeably lower than the first one. The graphical solutions of equation (31) at $T = \tilde{T}_K$ are presented in the upper panel of Fig. 5.

Thus, Kondo-type processes manifest themselves as a shake-up effect with a shake-up energy $\Delta_{v,c}$. They can be related to a final state interaction between the (e, h) pair in the dot and the Fermi continuum in the leads. The T -dependent logarithmic singularity in the exciton self energy is a precursor of an "orthogonality catastrophe", in close analogy with the corresponding anomaly encountered in connection with the self energy of a d -electron within the conventional Anderson model [17]. In the latter case the Kondo peak transforms to an undamped Abrikosov-Suhl resonance in the ground state [3,15]. However, this is not the case for the Kondo exciton (studied here) because of the finite lifetime τ_l of the (e, h) pair. The most important contributions to τ_l are given by the same tunneling processes which are responsible for the very existence of the midgap states. To take them into account one should include the states with

(e, h) pairs in the leads in the Green function expansion. Consider first diagrams (c) in Fig. 3, which describe the damping of a hole in the presence of an electron in the dot. Insertion of these diagrams in the self energy Σ_{cc}^- (28) leads to the correction

$$B_{cc}^- = \int_{-D}^D \frac{\tilde{f}(\epsilon')d\epsilon'}{\pi} \left[\frac{\Gamma_{vv}}{\epsilon + \epsilon' - \epsilon} + \frac{2\Gamma_{cc}}{\epsilon + \epsilon' - \epsilon + \Delta} \right]. \quad (34)$$

Estimating these integrals near the singular point $\epsilon - \epsilon_F \approx -\epsilon_v$, we find that this correction results in an insignificant renormalization of the v -level position, that is,

$$\delta\epsilon \sim \left(\Gamma_{cc} \ln \frac{|\epsilon_f - \Delta|}{D + \Delta} + \Gamma_{vv} \ln \frac{\Delta_v}{D} \right). \quad (35)$$

The valence level remains undamped in the case shown in fig. 4. In the general case of metallic lead with wide conduction band the damping is given by the diagram (c) of Fig. 3 with intermediate state "0" in a central loop (the first term in the r.h.s. of eq. 34). The lifetime is determined by $\text{Im}B_{vv}^- \sim \Gamma_{vv}$, and the peak at $\epsilon \sim \Delta_v$ survives, provided $\Gamma_{vv} < \tilde{T}_K$, i.e. $2\pi\Delta_c/\Gamma_{cc} < \ln D/\Gamma_{vv}$. The last restriction is not too rigid when the condition (29) is valid.

Turning now to the second peak at $\epsilon \sim \Delta_c$ (Fig. 4), we see that its existence is limited by the damping effects which are contained in diagrams (c) of Fig. 3. The corresponding correction to the self energy Σ_{vv}^+ is given by the integral

$$B_{vv}^+ = \int_{-D}^D \frac{f(\epsilon')d\epsilon'}{\pi} \left[\frac{\Gamma_{cc}}{\epsilon - \epsilon' + \epsilon} + \frac{2\Gamma_{vv}}{\epsilon - \epsilon' + \epsilon - \Delta} \right]. \quad (36)$$

In this case the damping $\text{Im}B_{cc}^- \sim \Gamma_{cc}$ is fatal for the resonance because $\Gamma_{cc} > \tilde{T}'_K$.

It has then been demonstrated above that in the case of well localized hole states in the dot the midgap exciton arises at $\epsilon \sim \Delta_v$ provided the inequalities (29) are satisfied. The crucial role of lifetime effects is especially manifested in the opposite limit of completely symmetric configuration $V_c = V_v$, $\Gamma_{ij} \equiv \Gamma$, $\Delta_c = \Delta_v \equiv \Delta/2$. In this case Σ_{0e} vanishes identically, and the secular equation (25) becomes

$$\epsilon - \Delta - \Sigma_{ee}(\epsilon) = 0. \quad (37)$$

Now $\text{Re}\Sigma_{ee}(\epsilon)$ diverges at $T \rightarrow \tilde{T}_K = D \exp(-\pi\Delta/2\Gamma)$. As a result a peak arises in $\text{Im}G_{ee}$ at ϵ around $\Delta/2$ provided the lifetime effects are not taken into account. When the particle-hole symmetry is slightly violated ($\delta \neq 0$), $\Delta_c = \Delta/2 - \delta$, $\Delta_v = \Delta/2 + \delta$, $\delta \ll \Delta/2$, this midgap peak disappears with increasing δ due to cancellation of singular terms with opposite signs in eq. (25).

This midgap state is also fragile against the lifetime effect. In a symmetric case (37) the self energies $B^\pm(\epsilon)$ have imaginary parts $\approx 2\Gamma$ at $\epsilon \approx \Delta/2$ which completely smear the peak structure. Thus, the Kondo processes initiated by one of the partners in the electron-hole pair are killed by the damping of its counterpart due to the same tunneling mechanism.

Focusing on a more promising asymmetric case (29), we find that the main peak of optical transition at $h\nu = \tilde{\Delta}$ is accompanied by a satellite peak at $h\nu \approx \Delta_v$. The form of this peak is determined by eq. (16), i.e., by

$$\frac{1}{\pi} \text{Im} G_{ee}(h\nu) = \frac{1}{\pi} \text{Im} \left[h\nu - \Delta - \tilde{\Sigma}_{ee}^-(h\nu) + i\hbar\tau_l^{-1} \right]^{-1}, \quad (38)$$

where $\tilde{\Sigma}_{ee}^-$ is given by the r.h.s. of eq. (32). The line-shape $W(h\nu)$ strongly depends on T/\tilde{T}_K and τ_l [12,17]. If the tunneling gives no contribution to τ_l , like in the case illustrated by fig. 3, the limiting factor is the recombination time of confined exciton in the dot. This time is measured, e.g., in nanosize Si clusters embedded in amorphous SiO_2 matrix, and the experimentally estimated value is $\tau_l \sim 10^{-6}$ s for the singlet exciton [19]. Therefore, Kondo-type processes can survive in these systems if $\tilde{T}_K \gg 10^{-9}$ eV. Since \tilde{T}_K falls rapidly with increasing Δ_c , this condition imposes limitations on the value of the ration $r \equiv 2\pi\Delta_c/\Gamma_c$: the shake-up sideband or satellite of the exciton peak in luminescence spectra can be observed at $r < \ln(D/h\tau_l^{-1})$. Taking $D \sim 1\text{eV}$, implies the restriction $r < 30$. Since the tunneling rate through the junction SQD/metal can be made large enough (e.g., $\Gamma_c \sim 0.05$ eV for InAs/gold tunnel barrier [20]), this restriction is not insurmountable.

Figure 5 illustrates the evolution of satellite peak in excitonic spectrum with changing position of the level ϵ_c . The graphical solutions of eq. (31) for a Kondo temperature \tilde{T}_K are shown in the upper panel. Here the value of $\Gamma_c/2\pi = 0.01D$ is chosen and the hole life time is not taken into account. It is seen from these solutions that the Kondo temperature rapidly falls from $\tilde{T}_K \approx 1 \cdot 10^{-7}D$ for $\Delta_c = 0.15D$ (solid line) to $\tilde{T}_K \approx 1 \cdot 10^{-16}D$ for $\Delta_c = 0.30D$ (dashed line). Due to the lifetime effects mentioned above the latter solution is inachievable, but the secondary shoulder or satellite of the main excitonic peak arises in a first case. (lower panel of Fig. 5). This panel illustrates the temperature dependence of optical line-shape calculated by means of eq. (38). We have taken the value of $\hbar\tau_l^{-1} = 5 \cdot 10^{-9}D$ in these calculations. The shake-up satellites are seen distinctly at temperatures as high as $T \approx 10^2\tilde{T}_K$.

It is worth stressing here that the exciton spectrum has been analyzed within the simplifying infinite- U approximation. In particular, it does not take into consideration charged states with two electrons or holes in the dot. Taking into account finite U means an inclusion of dou-

bly occupied states $|2c\rangle, |2v\rangle$ in the set (8), (11). In close analogy with the procedure adopted for the conventional Anderson model [15], one expects a redistribution of the spectral weight of neutral states $|0\rangle$ and $|es\rangle$ in favor of states $|2c\rangle, |2v\rangle$, and an increment of \tilde{T}_K with decreasing U . However, the inequality $\tilde{T}_K \ll \Delta_v$ ensures the existence of the midgap states as discussed above.

V. FURTHER APPLICATIONS OF THE MODEL

When formulating the generalized Anderson tunnel Hamiltonian with electron-hole branches of excitations in a dot, the natural candidates for its realizations are semiconductor nanoclusters. In this section some other physical systems for which many-body satellites of exciton lines can arise are briefly discussed. It has been established above that significant shake-up effects are expected in the process of exciton transition provided that: a) confined electron-hole pairs form a discrete spectrum with large enough separation between the first and subsequent levels, b) the Coulomb blockade is strong enough to satisfy the inequalities (6), and c) the hole states are only weakly damped. Evidently, SQD and wells containing transition metal (TM) impurities satisfy these conditions. TM impurities modify the electronic spectrum of semiconductor in such a way that the deep levels appear in the energy gap [21]. These levels are generated by d-states of unfilled 3d shell of TM ions which are substitution impurities characterized by the configuration d^n in the ground (neutral) state. In spite of strong covalent effects which mix the impurity d -states with Bloch waves pertaining to the host material bands (predominantly, with valence p -states), these levels retain the $l = 2$ angular symmetry modified by the cubic crystalline environment, and remain localized within 2-3 coordination spheres around the impurity site. Such TM impurity can bind an electron-hole pair. Usually, either electron or hole appear in the 3d-shell, and its counterpart is loosely bound by the Coulomb potential of ionized atom [22]. Thus, the processes of electron-hole pair capture can be represented as reactions $d^n \rightarrow [d^{n-1}e]$ or $d^n \rightarrow [d^{n+1}h]$ ("donor" and "acceptor" exciton respectively). Both types of excitons are observed experimentally in bulk II-VI semiconductors doped by various TM impurities (see [22] for a review of experimental and theoretical results). The scheme of energy levels of a TM-bound donor exciton in a heterostructure with a band offset $\Delta\epsilon_b$ is presented in Fig. 6 where the internal layer is selectively doped by 3d ions. Such heterostructure can be formed, e.g., in a three-layer sandwich CdSe/ZnTe/CdSe. The central layer should be doped by, e.g., Cr which is known to create a donor exciton in CdSe [21,22]. Here the deep level ϵ_d is the energy of transition $d^n \rightarrow d^{n-1}$ in the impurity 3d shell. The shallow level near the bottom of

the conduction band, ε_b , of the central layer is occupied by an electron bound to the positively charged $3d^{n-1}$ ion and *confined* in a barrier formed by the conduction band offset $\Delta\varepsilon_b$. In order to prepare the conducting leads, they should be heavily doped with n -type shallow impurities.

Since the states $d^n e$ and $d^{n-1} e^2$ are unstable due to Coulomb repulsion effect, and all states including d^{n-2} configuration are highly excited on an atomic scale, the pertinent physics is faithfully encoded by the model Hamiltonian (1) where the term H_d (7) includes the donor exciton described above. Apparently, the wavefunctions of electrons in the d -shell do not overlap with the band electron states in the leads. On the other hand, these band electrons can tunnel between the leads through the resonance shallow level ε_c of the confined electron. Hence, the properties of this system correspond to the case discussed at the beginning of Section IV, and one can expect the appearance of a satellite exciton at an energy $\Delta_V = \varepsilon_F - \varepsilon_d$.

Another possible realization of our model is exposed when mixed valent rare earth atoms are adsorbed on a metallic surface (hereafter they are referred to as adatoms). It is known that the Anderson model can be applied to adatoms with strongly interacting electrons (see [23] for a review). In this case H_t (12) corresponds to covalent bonding between an adatom and a substrate, V is the corresponding hybridization integral between the electrons in the adatom and those in the nearest sites of the metallic surface layer, and U is the intra-atomic Coulomb repulsion which prevents charging of the adatom in the process of chemisorption. The model was originally proposed for hydrogen atoms adsorbed on surfaces of transition metals [24]. Later on, the possibility of Kondo-type spin polarization of substrate electrons around an adatom spin in the case of $U \gg V^2/D$ was discussed [25]. The most promising candidates from the point of view of exciton effects are adatoms with unstable valence, e.g., Sm, whose ground state electronic configuration is $4f^6 6s^2$. Sm atoms can indeed be adsorbed on surfaces of transition metals such as Ni, Co, Cu, Mo. In the process of adsorption, a Sm atom loses its s -electrons and exists in two charged states Sm^{2+} and Sm^{3+} depending on the concentration of Sm ions on the surface. In particular, isolated ions $\text{Sm}^{2+}(4f^6)$ are observed on Mo surface at low submonolayer coverage [26]. The unfilled $4f$ shell forms a resonant f -state close to the Fermi level of the metal. The excited $5d$ state forms another level above ε_F . Thus, one arrives again at a two-level system described by the Hamiltonian H_d (3). Since the ground state term of the configuration $4f^6$ is a singlet 7F_0 , one cannot expect the occurrence of Kondo coupling for such adatom. However, in the course of virtual transitions between the adatom and the substrate the states $|kv\rangle$ and $|kc\rangle$ appear with excess electron e_k above ε_F (configuration $4f^5 e_k$) and a hole h_k below ε_F (configuration $4f^5 d h_k$). According to our calculations, one can excite

not only the conventional atomic excited state with energy $\Delta = E(4f^5 5d) - E(4f^6)$ but also the midgap states with energy close to $\Delta' = E(4f^5 e_F) - E(4f^6)$ where e_F refers to electrons on the Fermi level of the substrate.

VI. CONCLUSIONS

To summarize, this work suggests a generalization of the Anderson impurity model for semiconductor quantum dots in contact with metallic leads. This model takes into account the exciton degrees of freedom which are absent in a standard theory, and the spectrum of neutral excitation involves not only the electron-hole pairs confined within the dot, but also states in which one of the carriers appears in the leads in a process of tunneling. As a result, the model exhibits precursors of a Kondo effect pertaining to an excited state of an even- N SQD, despite the absence of Kondo coupling in the ground state. The theory developed here has an immediate experimental prediction, namely, that satellite exciton peaks of a Kondo origin can be detected in the optical absorption or luminescence spectra of SQD.

Attention in this paper was focused on the optical properties of SQD, whereas the physics of tunneling transport through these dots is expected to manifest specific features as well. Evidently, occurrence of midgap resonances of exciton type can not noticeably influence the single-electron or single-hole tunnel conductance of SQD, but anomalies in two-particle transport can exist. Novel features might be expected in luminescence relaxation spectra and the corresponding photocurrent. Moreover, an anomalous energy transport due to electron-hole cotunneling through SQD is also possible. In particular, investigation of frequency dependent photocurrent seems to be our next objective.

It is useful to point out once more that the case studied here refers to SQD with wide forbidden gap. The energy of excited neutral dot is higher than the energy of a singly charged dot. Such SQDs exist in a form of nanosize semiconductor droplets. Another type of quantum dots which is created near heterostructure interfaces by means of external gate voltage is an example of the opposite limit of complete Coulomb blockade, when the charging energy is much higher than the energy of the confined exciton. Our studies show that unusual Kondo type effect are possible in both cases. The difference is that in the first case, these effects appear as shake-up processes in excited states, and manifestations of many-body resonances are limited by the finite life time of the confined excitons, whereas in the second case a Kondo-type ground state can emerge provided triplet excitons are involved in the tunneling processes, and hence, spin-flip transitions become possible.

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Figure Caption

Fig. 1. Building blocks of the Green function expansion and the secular equation (25). The arrows indicate the tunneling processes which connect different states of this set.

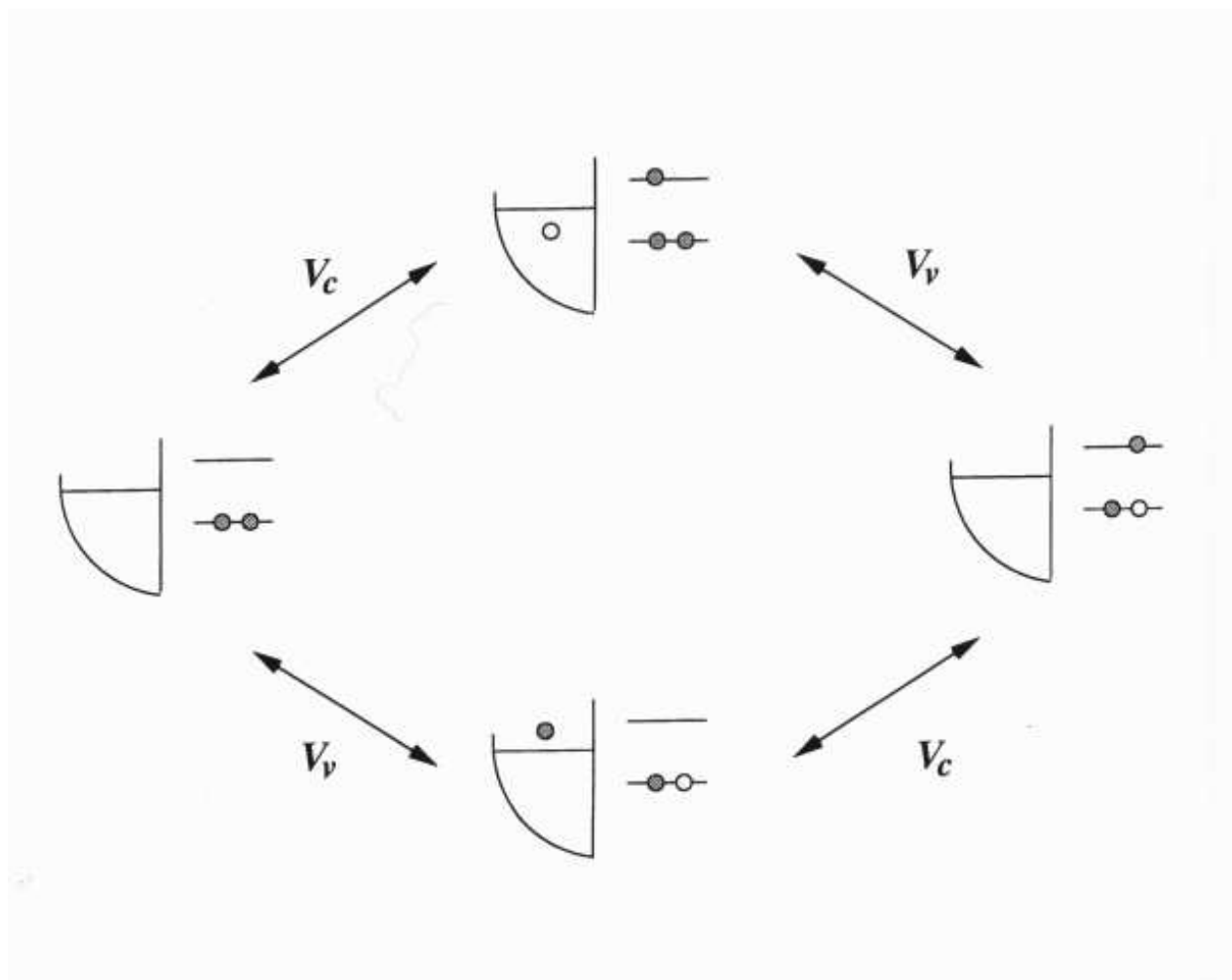
Fig. 2. Vertices, which couple the ground state $\langle 0|$ and the singlet exciton $\langle es|$ with the electron-hole pair states $|kc\rangle, |kv\rangle$

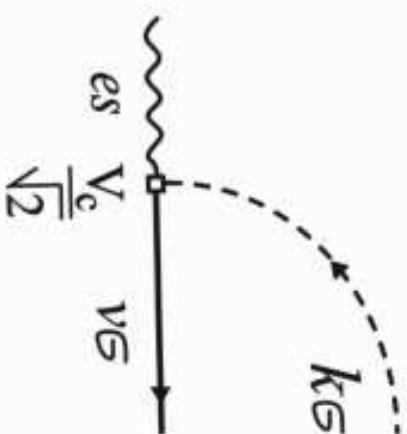
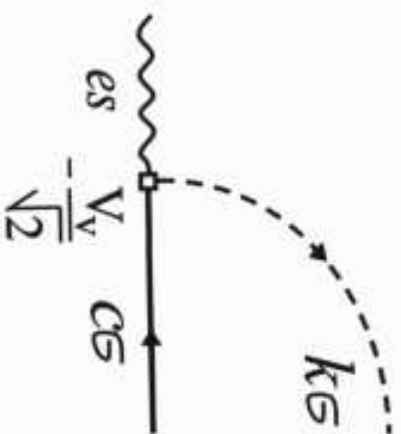
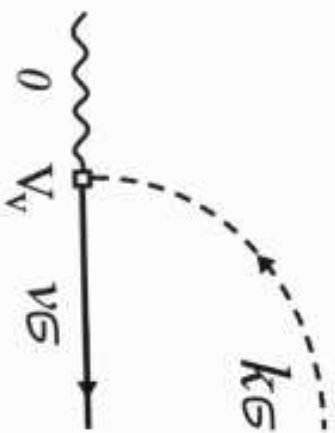
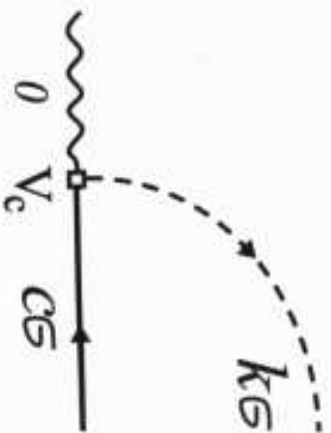
Fig. 3 Second and fourth order diagrams for singlet exciton self energy Σ_{ee}

Fig. 4. Energy levels of SQD coupled with degenerate n -type semiconductor

Fig. 5. Upper panel: Graphic representation of eq. 31 at $T = \tilde{T}_K$. $\tilde{\Sigma}_{ee}$ is the right hand side of eq. 31. $\Delta_c = 0.15D$, $\Delta_v = 0.85D$ (solid line), $\Delta_c = 0.3D$, $\Delta_v = 0.7D$ (dashed line). Lower panel: Optical line-shape W calculated from eq. (38) for $\Delta_c = 0.15D$. $T = 10^2 \tilde{T}_K$ (dashed line), $T = 5 \cdot 10^2 \tilde{T}_K$ (solid line). W_0 is the maximum value of W .

Fig. 6. Structure of electron bands and bound exciton states in a heterostructure formed by a central layer of semiconductor doped by TM impurities and the left and right layers formed by n -doped semiconductors.

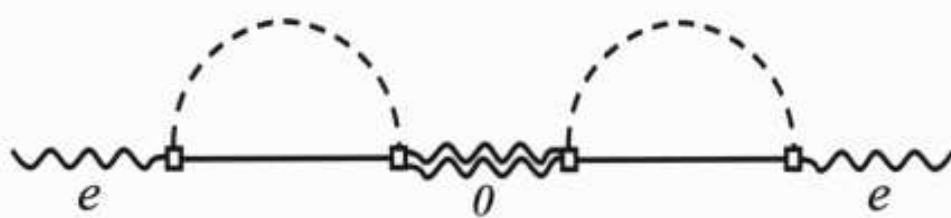




(a)



(b)



(c)

